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ELECTRODEPOSITION OF TANTALUM AND TANTALUM-CHROMIUM ALLOYS

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) As a part of a program to develop erosion resistant coatings for advanced gun barrels, electrodeposition of tantalum and tantalum-chromium alloys from fused FLINAK (eutectic mixture of LiF-KF-NaF) has been investigated. Tantalum-chromium alloys containing 2-6% chromium were obtained by codepositing tantalum and chromium from an electrolyte containing 10 wt% TaF ₅ (added as K ₂ TaF ₇) and 0.5-1.5% Cr (added as CrF ₃), at 800°C and 15-40 ma/cm ² current density. The alloy coatings were smooth and columnar in structure. The microhardness of these coatings increased with the increase of chromium content.			

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INTRODUCTION

Advanced gun barrels are required to fire propellants with increasingly high flame temperatures and at severe firing schedules, and therefore suffer from serious erosion in the critical area of the origin of rifling. One way to protect¹ the bore surface from excessive erosion is to use a liner or a coating of a material which must have a m.p. higher than gunsteel and good high temperature strength. It should also be resistant to the reactive propellant combustion gases and thermo-mechanically compatible with the main gunsteel body. In the case of a coating, it should not only be erosion resistant and well bonded with the substrate, but should also have an optimum thickness to protect the substrate from the effect of heat which is the cause of degradation of its mechanical strength.

Presently, chromium, which is an excellent erosion resistant material and can be electroplated from aqueous electrolytes, is being used in large and small caliber guns but it has serious limitations. In as plated condition it is full of microcracks and is extremely brittle. After a certain number of rounds it chips and flakes off, affecting adversely the performance of the gun. Other potential metals include Ta, Cb, W and Mo and their alloys. Their use as homogeneous liners is cost prohibitive. Therefore, their application as coatings is being seriously considered. Unfortunately, none of them can

¹I. Ahmad, P. Greco, G. D'Andrea, J. Barranco, "Potential Erosion Resistant Refractory Metal (And/Or) Alloy Coatings for Gun Tubes," Proceedings 1978 Triservice Conference on Corrosion, MCIC-79-40, May 1979, pp. 203-217.

be electroplated from aqueous electrolytes like chromium. Chemical vapor deposition, in general, requires very high temperature of deposition and the deposits have a tendency to pick up impurities thereby making them hard, brittle, and weak. In limited applications physical vapor deposition has been successfully used, but this technique works well as long as the coating is thin. In gun barrels thick coatings are required. Also, the large l/d ratio of gun tube or a liner, and the presence of rifling present serious problems. Diffusion coating processes such as metallizing² also give only thin coatings. Plasma spraying yields thick coatings, but they are porous and poorly bonded with the substrate.

Electrodeposition from fused salt electrolytes, described for the first time in 1954 by Senderoff and Brenner³ for molybdenum and later by Mellors and Senderoff^{4,5} in the form of a general technique for the majority of refractory metals (Ta, Nb, Zr, W, Mo, Cr, and V), is the most practical method which can yield thick, high purity, coherent and dense coatings. The process consists essentially of electroplating from a bath composed of fluoride compound of the refractory metal dissolved in a fused eutectic mixture of LiF, KF and NaF (Flinak) in the temperature range of 650-850°C and current density range of 5-125 ma/cm². Further work in this area reported during the

²N. C. Cook, "Corrosion Resistant Coatings," U.S. Patent 3024 176 (1962).

³S. Senderoff and A. Brenner, J. Electrochem Soc., 101, 16 (1954).

⁴G. W. Mellors and S. Senderoff, J. Electrochem Soc., 112, 266 (1965).

⁵G. W. Mellors and S. Senderoff, U.S. Patent 344058 (1969), Canadian Patent 688546 (1963).

last 15 years is related to the study of the electrode kinetics of Ta,⁶ Cb,⁸ and Zr⁷ in these processes, and the effect of impurities on the structure of these coatings. The major application of this general process developed during the last decade is the electrodeposition of tantalum by GMTC (Richmond, VA) in various components related to the chemical industry. GMTC in the USA is the sole license of the patent which is owned by Union Carbide. In Germany Degussa RFA reportedly¹⁶ has facilities to plate Ta, Cb, W and Mo.

One of the authors in collaboration with the GMTC has demonstrated the feasibility of applying 125 micron thick coating in 20 mm rifled liners. It is necessary to use a short liner which can be coated independently of the main tube, because exposure of gunsteel to the plating temperature (750-800°C) makes it very soft and lose its mechanical strength. This also means that the liner should be of a material which retains its yield strength at elevated temperatures. Because of the good throwing power of the process, the coating of a uniform thickness both on the lands and the grooves can easily be obtained. Figures 1(a) and 1(b) show a borescope view of the coated barrel and the magnified view of the transverse section of this coating. These

⁶S. Senderoff, G. W. Mellors and W. J. Rinehart, J. Electrochem Soc., 112, 840 (1965).

⁷Ibid, 113, 60 (1966).

⁸Ibid, 113, 66 (1966).

¹⁶J. Wurm, "European Conference on the Development of Molten Salts Applications," Extended Abstracts and Proceedings, pp. 62-69, Battelle-Geneva, September 1973.

liners on test firing¹⁰ in an M24A1 gun using a severe firing schedule proved tantalum to be an excellent erosion resistant material. However, in as plated condition tantalum is very pure and soft (180-250 KHN) and was found to swage by the engraving stresses of the projectile. It was therefore decided to investigate the possibility of improving the hardness of this coating by alloying with a few percent of chromium. Alloying with chromium up to 5-15% has been reported¹¹ to improve the oxidation resistance of columbium. Because of the similarity of Cb with Ta, the latter is expected to equally benefit with respect to resistance to oxidation by the addition of Cr. As has already been stated, chromium is known to be an excellent erosion resistant material as such; it was hoped that extension of this study would also lead to the optimization of conditions for electrodeposition of pure chromium and Cr-Ta alloys.

Senderoff and Mellors⁵ report the electroplating of chromium from Flinak bath using 8% CrF_3 as a source of soluble chromium, and an anode composed of chromium chunks in a nickel basket. Current densities of 25-60 ma/cm² and temperatures of 800-840°C were used. They recommended K_3CrF_6 as the preferred salt. Few details were given. Chromium electrodeposition from fused fluorides using $\text{CrF}_3 \cdot 4\text{H}_2\text{O}$ ¹² also has been attempted but only powdery deposits on graphite

⁵G. W. Mellors and S. Senderoff, U.S. Patent 344058 (1969), Canadian Patent 688546 (1963).

¹⁰R. Cullinan and G. D'Andrea, "Erosion Study of Tantalum Coated Gun Barrels," To be presented at 1980 JANAF Meeting.

¹¹W. Klopp, "Oxidation Behavior and Protective Coatings for Columbium and Columbium Base Alloys," DMIC Report 123, January 1960, BMI, Columbus, OH, pp. 43-44.

¹²S. Marion and J. L. Andrieux, Compt. Rend. 242, 2903 (1956).

electrodes were obtained. Bowles and Newdick¹³ used 2% CrF_2 for chromizing mild steel. Tarasova¹⁴ reported successful plating of chromium from LiF-NaF melt containing 5-20% K_3CrF_6 , using 10-100 ma/cm^2 current density and 700-900°C temperature. Plating thickness was limited to 200-250 microns. Mellors and Senderoff⁵ also report one experiment in which Ta-Cr alloy was deposited from a melt containing 7.4 wt% TaF_5 and 0.3 wt% CrF_3 , at a current density of 25 ma/cm^2 and a temperature of 775°C. A hard plate of 99% Ta containing 1% Cr was obtained. No other details are given.

In this study, first the conditions for the deposition of pure Ta (in the lab) were established, and then the effect of the addition of chromium (by codeposition) on the structure and microhardness of the Ta coating was determined. A few preliminary runs to deposit Cr and Cr-rich-tantalum alloys were also made. The paper discusses some of the results obtained.

EXPERIMENTAL

Chemicals and Materials

Anhydrous, powdered reagent grade LiF , NaF , KF , K_2TaF_7 and CrF_3 were vacuum dried at 180°C for 100 hrs and stored in vacuum dessicator until needed. K_3CrF_6 was synthesized¹⁵ by fusing Cr_2O_3 with KHF_2 (1:6 ratio) in

⁵G. W. Mellors and S. Senderoff, U.S. Patent 344058 (1969), Canadian Patent 688546 (1963).

¹³P. J. Bowles and P. C. Newdick, "Electroplating and Metal Finishing," 24, 6 (1971).

¹⁴K. P. Tarasova, A. N. Boraboshkin, and M. Yanoya, Tr. Inst. Elektrokhim Ural Nauk Tsentr Akad Nauk SSSR 17, 118 (1971).

¹⁵O. T. Christensen, J. Prakt. Chem. 35, 161-3 (1887).

a platinum crucible (contained in a graphite crucible with a graphite cover) and maintained in the molten state for ten minutes. The mixture was allowed to cool, then extracted three times with a 5% HF (aqueous) solution. The resultant product was insoluble and paris green in color. It was pulverized, vacuum dried at 180°C for 72 hrs and then stored in a dessicator. High purity argon (99.999%) was used for inert atmosphere throughout this study.

Anodes: Tantalum and chromium metals were used as soluble anodes. Tantalum anode was machined from a 3 mm thick unannealed metallurgical grade plate. Prior to electroplating it was etch-cleaned for five minutes in a 2:5:1 solution of concentrated HAC:HCl:HF which produced a bright clean finish. Chromium anode was in the form of discs which were cleaned with a 3:1:4 solution of H₂O₂:HCl:H₂O.

Cathodes: Copper metal (3.2 mm x 12.5 mm x 50 mm) and 304 stainless steel (3.2 mm x 11 mm x 50 mm) coupons were used as cathodes. They were ground (to 400 and 600 grit finish) and etch cleaned with 1:1 H₂O:HNO₃ and 3:27:70 KNO₃:H₂SO₄:H₂O solutions respectively. All etched electrodes were cleaned with distilled water, dried at 110°C and stored in a dessicator until used.

Electrolytes: LiF, NaF, and KF were mixed in a molar ratio of 46.5:11.5:42.0 respectively, to obtain the ternary eutectic which had a melting point of 454°C. The mixture was ground and vacuum dried at 150°C until a residual pressure of 1.5×10^{-2} mm Hg was obtained. It was premelted in a vitreous carbon crucible under argon and kept at 600°C for 20-30 minutes, cooled to just above the melting temperature and then decanted into an etch-

cleaned pure nickel crucible. The melt appearance was from water clear to light yellowish in color. After cooling the crucible, the ternary eutectic was then transferred into a vacuum glass envelope, heated externally by a resistance tube furnace and slowly heated to 450°C under vacuum. Argon gas was then introduced in the envelope and the temperature was raised until complete fusion occurred. The assembly was then slowly evacuated to remove all dissolved gases. The temperature was gradually raised (taking care that no splattering occurred) up to 800°C and maintained under vacuum for 48 hrs. The system was then slowly cooled under vacuum and filled with pure argon. Sometimes there was a layer of dark surface film on the solidified eutectic which was scrapped in a glove box. The electrolyte prepared in this manner was used for studies of electrodeposition of tantalum. For experiments on Ta-Cr alloys, the eutectic mixture was simply premelted under dry argon, cooled and used as such without vacuum degassing steps. The suppliers of the materials are listed in Table I.

Electroplating Assembly

The electrolytic cell assembly is illustrated in Figure 2. It consisted of two parts. The lower part to hold the crucible (1), containing the electrolyte, was an all welded stainless steel cylinder (2). The upper part (3), the "head" had the various ports to provide access to the cell interior for the electrodes, and the inert gas atmosphere. The two parts were coupled with a stainless steel flange (4) containing a high vacuum copper gasket. Cooling coils (5) were used around the flange to keep the temperature of the copper gasket and the head, in general, low. This allowed the use of slip

seal at the electrode entry ports (6) for admitting the electrode leads to the hot zone. To assure a sound electrical connection the electrodes were attached to stainless steel suspension rods (7) by a platinum wire. The gate valve (8) enabled the isolation of the entry port from the cell after the cathode was withdrawn from the electrolyte at the end of the run. Entry port (9) was used for a reference electrode, when required. The bottom 160 mm of the plating cell was placed in a Lindberg crucible furnace (10). The furnace temperature was controlled with the Lindberg time proportioning temperature controller, which maintained the desired temperature to $\pm 10^{\circ}\text{C}$. The 140 mm hot zone of the furnace maintained the electrolyte at thermal equilibrium.

Electrodeposition of Tantalum

The general procedure used was as follows: The plating cell was loaded with the electrolyte contained in the nickel crucible and the preweighed electrodes. The assembly was evacuated and back filled with argon. Maintaining a steady flow of the inert gas, the cell was then heated to 450°C for six hours. To insure complete fusion, the temperature was then raised to 800°C and the cell was allowed to reach thermal equilibrium. Preweighed K_2TaF_7 was then added under argon atmosphere to the melt through the anode port. The cell temperature was brought to the desired plating temperature level and allowed to equilibrate for 48-72 hours. The anode was then positioned in the melt. To calculate the current density to be used, the depth to which the electrode was immersed in the melt was determined by withdrawing the cathode from the melt, into the entry port, closing the gate

valve, and measuring the position of solidified salt line from the bottom of the electrode. The electrode was reinserted into the melt. The electrolyte was then pre-electrolyzed at $40\text{--}50\text{ ma/cm}^2$ for one hour. The pre-electrolysis of the melt was considered complete when the voltage stabilized. The cathode coupon was withdrawn into the entry port and substituted with the proper cathode coupon, which was then lowered into the melt to the same depth as the dummy. Electroplating run was made at the predetermined current density using a Sargent coulometric current source. After the run, the sample was withdrawn and ultrasonically cleaned in distilled water for 1-3 hours to remove all adherent salts. The cathode was weighed. The area of the deposit was measured. The plating thickness was calculated from the weight gain and assuming theoretical density of the deposited metal. The specimen was then sectioned and polished for metallographic examination, electron microprobe analysis (EPMA) and microhardness measurements using the standard techniques.

At the end of some runs, the solidified electrolyte was analyzed to determine the valency of Ta and Cr in the melt. The total concentration were obtained by atomic absorption spectrometer (Perkin Elmer 403). Solution of the melt was made by dissolving it in 5% HF. From the stock solution aliquots containing 100-1500 micrograms of the melt were made and used for further analysis. In the case of Ta the solidified electrolyte was dissolved in the presence of FeCl_3 and titrated back against standard $\text{K}_2\text{Cr}_2\text{O}_7$ solution using barium dipheylamine sulphonate as indicator to determine the reducing power. The results were compared with total Ta concentration from atomic absorption analysis and the mean valency was calculated. For chromium,

the solidified melt was dissolved in excess EDTA solution and then titrated back with NiCl_2 solution using murexide as indicator. Again using these data and the total Cr concentration obtained from atomic absorption analysis, the mean valency of Cr was calculated.

RESULTS

Tantalum

The performance of the plating assembly was investigated by electro-deposition of tantalum under the following range of conditions:

Temperature	770-820°C
Current Density	5-45 ma/cm ²
Plating Bath Composition	FLINAK + 10 wt % TaF ₅ added as K ₂ TaF ₇

To achieve complete dissolution the electrolyte was equilibrated at 770°C for three hours. Stainless steel (304) coupons were used as cathodes. Pre-electrolysis for 0.5 hrs at 43 ma/cm² was found to remove most of the undesirable impurities. In the initial runs, "treeing", i.e., formation of long dendrites at the melt-electrode-argon interface was observed. This was overcome by equilibrating the solute in FLINAK at 800°C for as long as 72 hours. Also, it was found necessary to equilibrate the electrodes to a temperature as close as possible to the plating temperature before inserting them in the electrolyte. In a number of runs in which the purity of the melt or the atmosphere could not be maintained, low current efficiency and low deposition rate were obtained. As reported by previous workers, it was necessary to exclude all possibilities of contamination of the electrolyte from moisture,

atmospheric oxygen or air. The rate of deposition vs. current densities of about 20 runs made are plotted in Figure 3. Runs with low current efficiency are also shown as small crosses.

To ascertain the feasibility of plating a thick coating, such as may be required in gun barrels, in one sample 0.9 mm (36 mil) thick coating was obtained at a current density of 17.5 ma/cm^2 in 64 hours the current efficiency was 99.3%. Most of the coatings were smooth in appearance. Figure 4(a) is the transverse section of a typical coating, indicating dense columnar structure. The hardness profile of a similar coating is shown in Figure 4(b).

Tantalum Rich Tantalum-Chromium Alloys

The general procedure of plating was exactly the same as that used for tantalum, except that the plating temperature was 800°C . In three series of runs, SB, SC, SD, chromium to the extent of 0.5, 1.0, and 1.5% as K_3CrF_6 was added to the FLINAK bath containing 10 wt % of TaF_5 as K_2TaF_7 . The bath was equilibrated for 26 hours. Experiments were conducted at current densities in the range of $5\text{-}40 \text{ ma/cm}^2$. An average of nine runs were made in each series. Again, the surface coatings in general were smooth. The coating rates (mils/hrs) as a function of current density for the three series are shown in Figure 5. Traverse section of a typical alloy is shown in Figure 6, which indicates dense columnar structure not different from that of Ta coating. Selected specimens from the three series were sectioned, polished, and the variation of both microhardness and chromium content by electron probe microanalysis (EPMA) in the coatings were determined. EPMA analyses were made by scanning the coatings at 10 micron intervals from the substrates/plate inter-

face to the plate edge. Results are summarized in Table II. Figure 7 shows the hardness and composition profiles of a Ta-Cr alloy specimen (SD-3). An EPMA profile of tantalum at 2 micron interval across the interface in specimen SD-3 is shown in Figure 8, indicating a diffusion zone of about 10 microns. Figure 9 shows the variation of chromium in SB-6, SC-3, and SD-3 coatings. The sensitivity of the measurement of chromium content by EPMA technique was $\pm 0.5\%$.

Chromium and Chromium Rich Alloys

Limited number of runs were made to study the feasibility of plating Cr and Cr-Ta alloys. In the case of chromium, pieces contained in a nickel basket were used as an anode. Copper coupons were used as cathodes. The electrolyte was FLINAK containing 6 wt % CrF_3 . For Cr-Ta alloys, in addition to CrF_3 0.05 wt % TaF_5 as K_2TaF_7 was also added. For pure chromium deposition, current density in the range 0.8 - 49.9 ma/cm² and melt temperature of 800-835°C were evaluated. Unfortunately, in these runs the nickel from the basket tended to dissolve anodically in the melt. The coatings obtained were mostly dendritic and porous and the current efficiency was, in general, low. However, the hardness values in the nonporous areas of these deposits were in the range of 137-206 KHN indicating high purity chromium. The purity of Cr was confirmed by EPMA. Addition of 0.05 wt % TaF_5 gave coherent dense coating such as shown in Figure 10 which was obtained at a C.D. of 25.8 ma/cm². In 11 hours a thickness of 6.5 mil was obtained (current efficiency 65%). The average microhardness of the coating was found to be 294 KHN which is higher than pure chromium or tantalum. EMPA of this coating did not detect

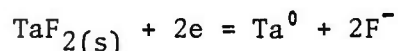
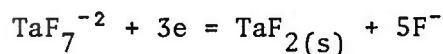
the presence of Ta. Apparently, the alloy contained less than 0.5% Ta which was the detection limit of EPMA. A noteworthy feature of this coating is that its structure is almost equiaxed instead of the usual columnar grains.

Melt - Analysis

Chemical analysis of the electrolyte from selected runs showed that the mean oxidation state of tantalum and chromium ions were respectively +5 and +2.7.

DISCUSSION

Initial runs of electrodeposition of tantalum essentially confirmed the results of Mellors and Senderoff.⁴ Dense, columnar and high purity (indicated by the microhardness similar to that of high purity bulk Ta) coatings were obtained at a current efficiency of almost 100%. The analysis of the electrolyte after numerous electroplating runs showed the oxidation state of tantalum in the melt to be +5 as reported by Senderoff, Mellors, and Reinhart, who suggested that the reduction of $(\text{TaF}_7)^{-2}$ takes place in the following two steps:



The first step is reversible (controlled by the diffusion of Ta^{+5}) and the second step is not diffusion controlled and is irreversible. The rate of

⁴G. W. Mellors and S. Senderoff, J. Electrochem Soc., 112, 266 (1965).

deposition as shown in Figure 3, up to about 30 ma/cm² is almost a linear function of current density and can be represented approximately by

$$(\text{mils})/\text{hr} = 0.03 \times \text{C.D.}$$

At higher current densities, only a few runs were made and it is not certain if the apparent deviation from linearity is due to polarization effects.

Very little on the alloy deposition from fluoride electrolytes has been reported in the literature. Present work shows that a homogeneous alloy coating of Ta-Cr can be obtained by the addition of Cr in the bath as CrF₃. The chromium content in the alloy is a linear function of the chromium added in the melt (Figure 11). For the same current density, the two elements should deposit in the ratio of their equivalent wts (i.e., 17.7:36). The deposition potentials of Ta and Cr in FLINAK electrolyte are very close ($E_{1/4}$ -1.126, -1.13 V). If their activities in the melt were also similar under steady state conditions they should deposit in the ratio of approximately 1 Cr:2 Ta. The ratios of Cr:Ta in the deposits from electrolytes containing 0.5, 1.0, and 1.5 Cr, were however, on the average 1:49, 1:19, and 1:14. Qualitatively speaking, the main reasons of the low ratios could be low initial Cr:Ta ratio in the melt and probably high activity coefficient of Cr in the melt because of some complexation.

From Figure 5 it appears that alloying with chromium did not noticeably change the rate of deposition of tantalum. However, as Table II shows, increase in the amount of chromium added to the electrolyte decreased the current efficiency from 99% to 74%.

Figure 9 further shows that the concentration of Cr is the highest at the coating-substrate interface (i.e., at the start of electrodeposition), and then it gradually decreases. This is reflected in the decrease in the hardness at the corresponding positions in the coating.

The hardness of the coating, as expected, increased with chromium content. The data are summarized in Figure 12. The bars indicate the variation of hardness across the specimens. This figure shows that it is possible to increase predictably the hardness of tantalum by the addition of small percentages of chromium. No high temperature hardness data were obtained at this time but it is expected that like other Ta alloys, Ta-Cr alloy will also maintain its hardness (or yield strength) at elevated temperature. This will be very beneficial for the gun barrel erosion control applications.

EPMA Scan for chromium in SD-3 (Figure 8), shows a diffusion zone of about 10 microns. The exact composition of the interface is not known at this time. It was harder than either the alloy or steel indicating some diffusion of carbon, but no distinct decarburized zone at the interface was detected by ordinary microscopy. Nevertheless, the bond between all these coatings and the 304 stainless steel substrate as shown by these micrographs was very good.

The experimental values for the oxidation state of +2.7 for Cr in the electrolyte may be an indication of the criticality of Cr ion valency in the melt. Whether this was a cause of low current efficiency and poor coating is not known at this time. Mellors and Senderoff suggest a value of +3 in their deposition of Cr experiments which reportedly were successful. The

presence of nickel ions in the melt and perhaps pretreatments which were less rigorous than those used for tantalum may also be responsible for poor quality. However, hardness measurements showed that in the dense areas the coating was quite soft.

An interesting aspect of these experiments was that by the addition of only 0.05% TaF₅, dense coating of Cr (with traces of Ta, which could not be detected by EPMA) was obtained. The increase of hardness to a value of 244 KHN, probably is due to the traces of Ta. Another feature of this coating is that unlike the usual columnar grain structure of the coatings from these electrolytes, the chromium-tantalum alloy has very fine grain size which is expected to have superior mechanical properties than the columnar type of deposits.

CONCLUSION

In addition to the confirmation of the results of Mellors and Senderoff on the coating of Ta from FLINAK, this study has shown that Ta-Cr alloys with predetermined chromium content can be obtained by the addition of CrF₃ to the electrolyte. The hardness of the alloy was found to be a function of chromium content in the alloy. This suggests that for gun barrel application Ta coatings of predictable hardness can be obtained. Further work is necessary to confirm if these coatings maintain the increased hardness at elevated temperatures, and also if addition of chromium, as expected, would improve the erosion resistance of these coatings.

Although impurities vitiated successful coating of pure chromium, and the process of Mellors and Senderoff described in their patent⁵ could not be confirmed, dense coatings of chromium were successfully obtained by the addition of traces of Ta, as TaF₅ to the electrolyte. Unlike the usual columnar structure of the coatings obtained from FLINAK, the Cr-Ta alloy had almost an equiaxed structure, which is quite desirable.

⁵G. W. Mellors and S. Senderoff, U.S. Patent 344058 (1969), Canadian Patent 688546 (1963).

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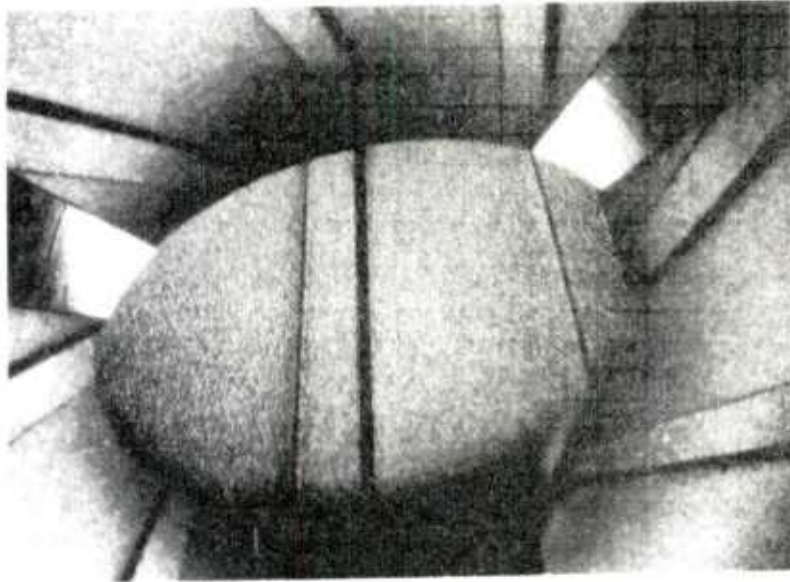
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TABLE I. SOURCES OF CHEMICALS AND MATERIALS

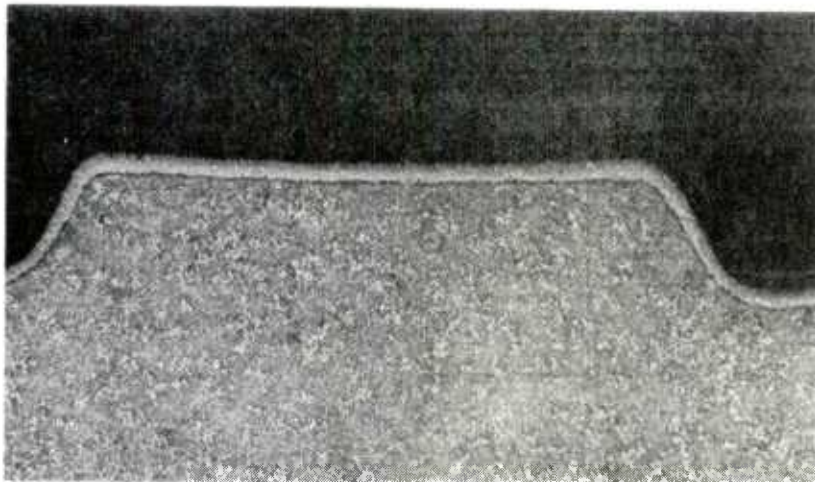
LiF, NaF	Fisher Scientific
KF	Baker Chemical Corporation
	Matheson, Coleman, and Bell
K_2TaF_7	Kawecki Berylco Industries, Inc.
K_3CrF_6	Synthesized
CrF_3	Research Organic
	Chemicals Corporation
Tantalum	Kawecki Berylco Industries, Inc.
Chromium	Alfa-Ventron Products

TABLE II. CONDITIONS USED TO ELECTRODEPOSIT Ta AND Ta-Cr ALLOY COATINGS

Specimen No.	Wt % TaF ₅	Wt % Cr Added as CrF ₃	Temp of Dep °C	C.D. ma/cm ²	Current Eff. %	Rate/hr Micron (mil)	Wt % Cr (EPMA)	Hardness KHN (50 gm)
SA 5	10	-	755 ± 20	17.5	99.3	13 (0.5)	-	217 ± 21
SA 15	10	-	755 ± 20	27.7	99.6	23 (0.9)	-	217 ± 21
SB 6	10	0.5	800 ± 20	18.7	92.2	14 (0.5)	2.2 ± 0.07	475 ± 21
SC 3	10	1.0	800 ± 20	36.7	89.4	23 (0.9)	4.7 ± 0.07	669 ± 30
SC 5	10	1.0	800 ± 20	29.1	88.2	20 (0.8)	4.67 ± 0.08	634 ± 27
SD 3	10	1.5	800 ± 20	20.4	74.4	13 (0.5)	6.6	772 ± 35



(a)



(b)

Figure 1. (a) Borescope view of a tantalum coated section of 20 mm barrel; (b) Transverse section of a land showing uniformity of the coating thickness.

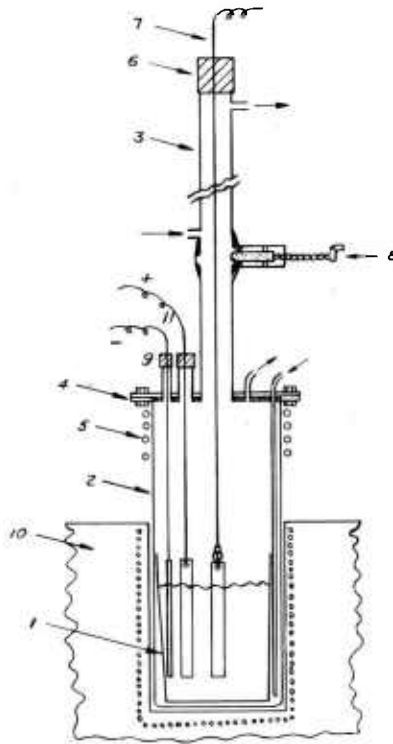


Figure 2. Electroplating cell assembly: (1) crucible, (2) stainless steel cell, (3) head, (4) flange, (5) cooling coil, (6) entry ports, (7) suspension rod for the cathode, (8) gate valve, (9) entry port for reference electrode, (10) Lindberg crucible furnace, and (11) entry port for anode.

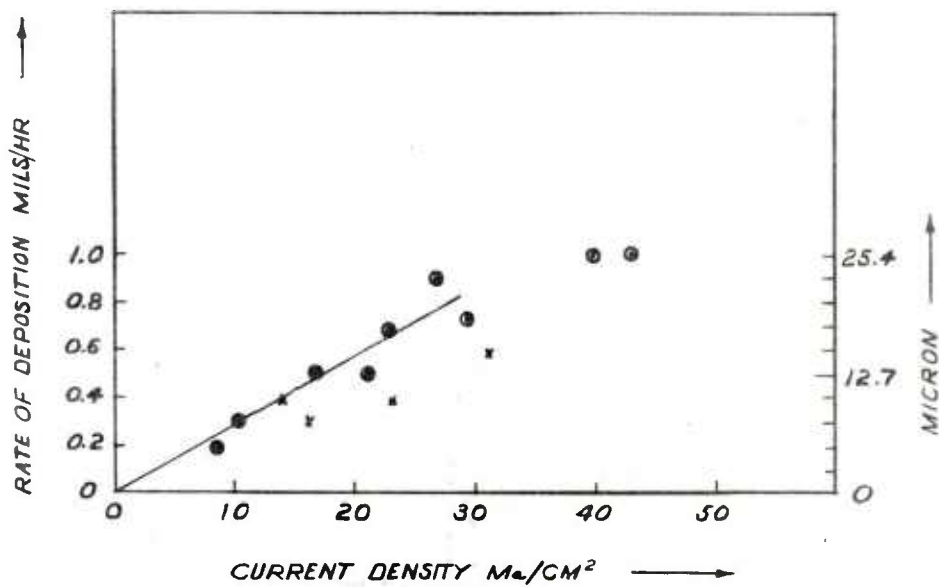
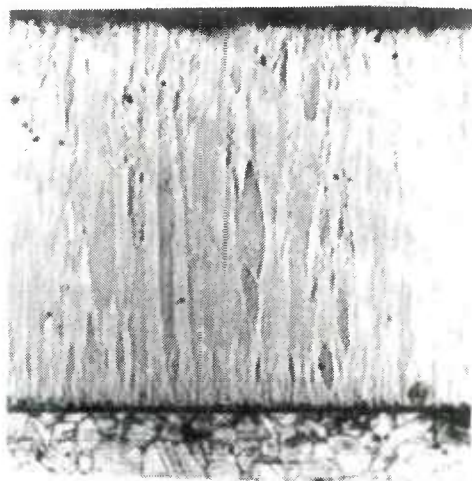
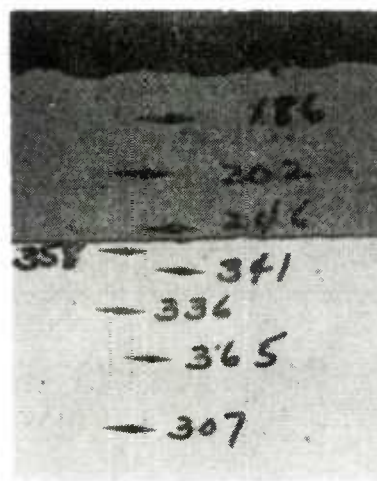


Figure 3. Rate of deposition of tantalum vs. current density. Runs with low current efficiency(x).



(a)



(b)

Figure 4. (a) Transverse section of a typical tantalum coating (X200). (b) Microhardness profile.

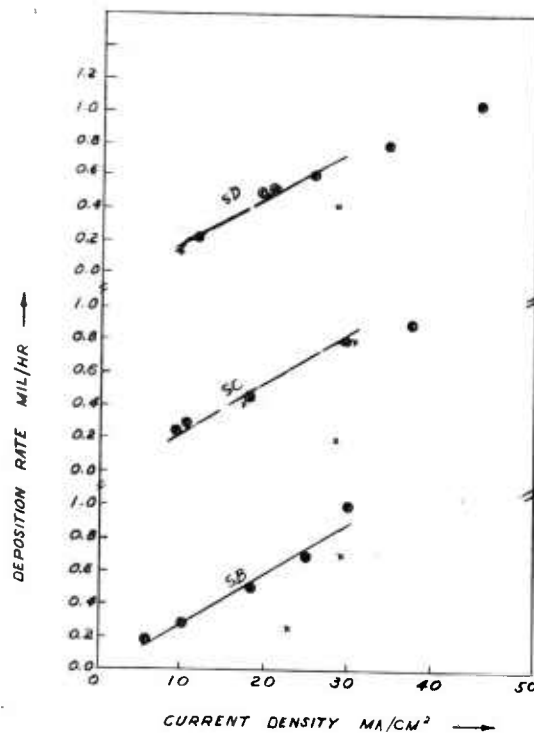


Figure 5. Ta-Cr alloy coating rates as a function of c.d. for three series of runs. Low current efficiency runs (x).

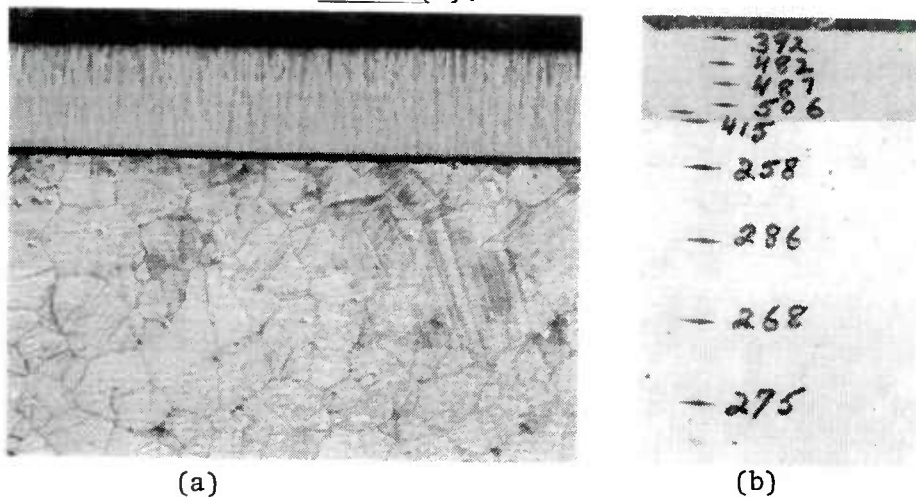


Figure 6. Transverse section of a typical Ta-Cr alloy coating. (a) 0.5 Cr SB-6 (X100), (b) hardness profile.

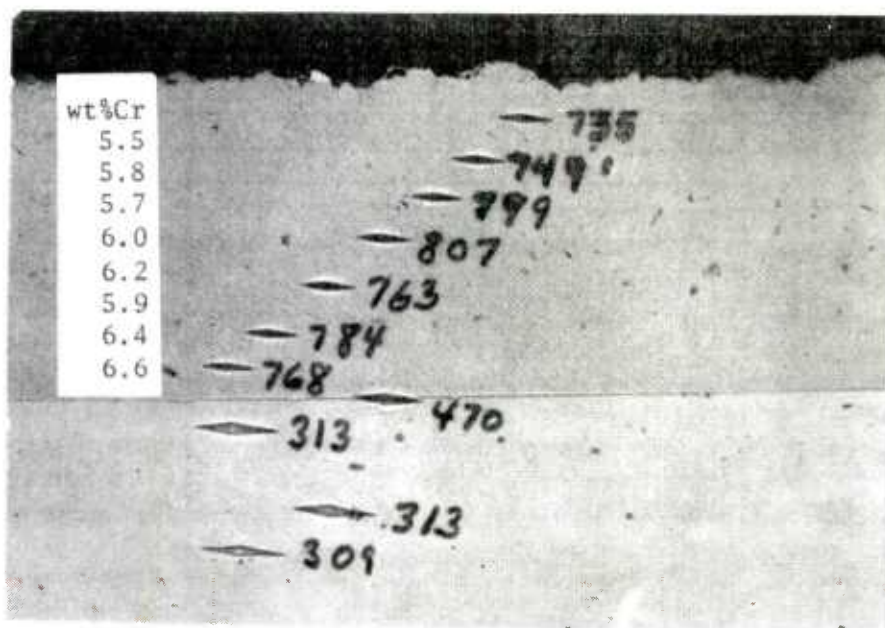


Figure 7. Hardness and Cr composition profile of a selected coating SD-3 (interval between data points 20 microns).

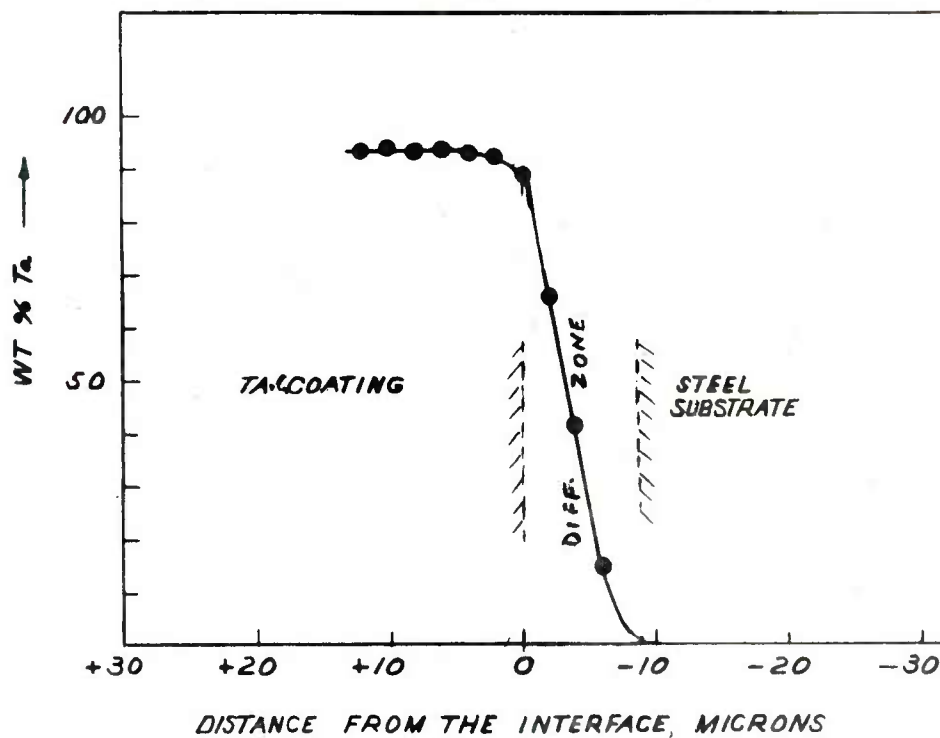


Figure 8. EPMA profile of Ta-Cr/steel interface in SD-3 specimen.

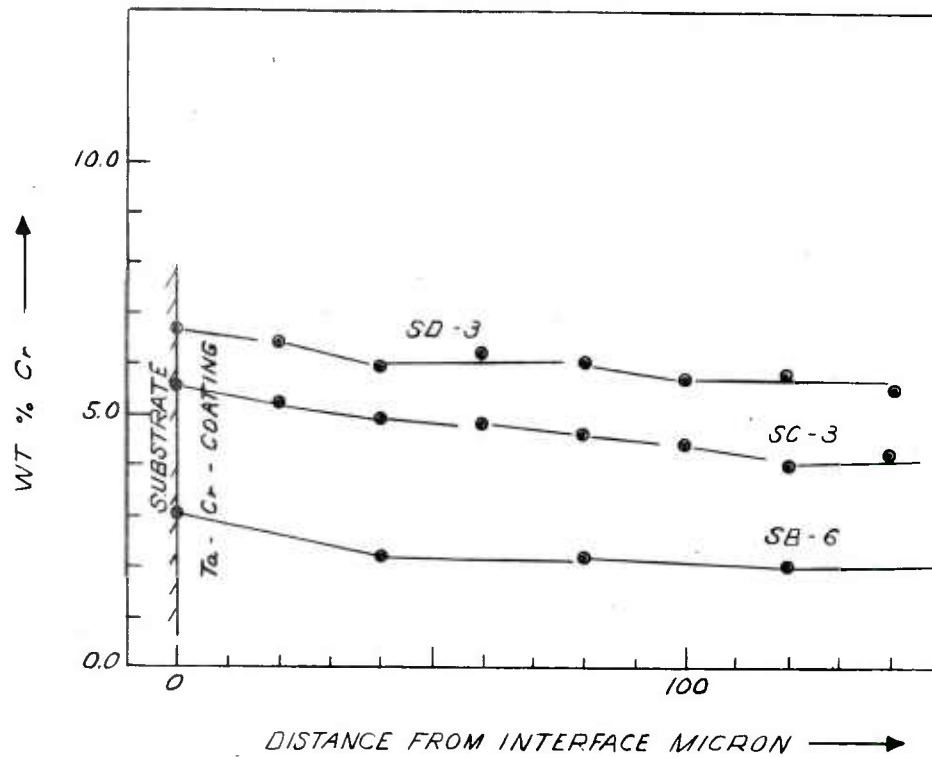


Figure 9. Variation of chromium in SB-6, SC-3, and SD-3 coatings.

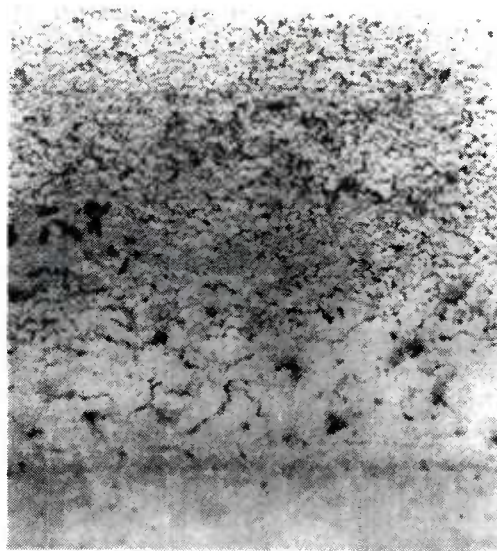


Figure 10. Cr-Ta coating, indicating equiaxed structure (X1000).

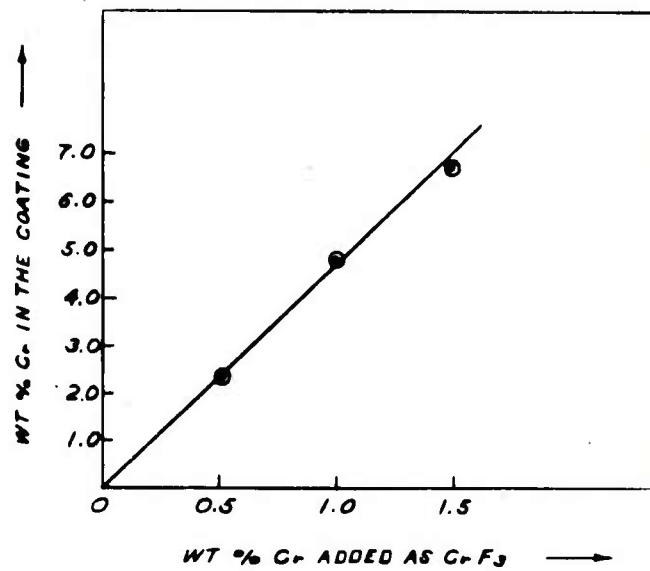


Figure 11. Variation of Cr in the coating as a function of Cr added as CrF₃ in the melt.

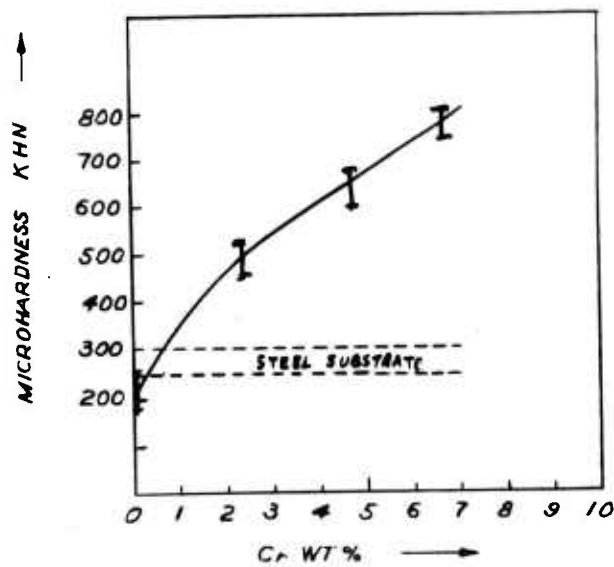


Figure 12. Variation of hardness of tantalum alloy with the chromium content.

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